



Vision/Impact

- **Vision: Advance the science of carbon-based materials**
 - Fundamental phenomena induced by unique microstructures
 - New generation of micro- and nano-multifunctional devices
- **Effectively couple existing programs on carbon-based materials**
- **New Science**
 - Nanoinstrumentation
 - Mechanical/Tribological/Electronic studies of Nanostructured Materials
- **Novel nanotechnologies**
 - Carbon-based MEMS processing techniques
 - Carbon Nanocomposites

Outline

- Project Participants, Management Plan & Budget
- Project Goals
- Project Activities (Since February 2002)
 - TEM nanoindentation studies of a-D and UNCD
 - Synthesis and field emission studies of carbon nanocomposites
 - Molecular dynamics study of UNCD Growth
- Planned Activities for the upcoming year
 - MEMS for mechanical, tribological properties
 - Low temperature growth
 - Diamond Stiction
 - Field emission
- Technological Applications and Industrial Partners
- Summary



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

3

Center Participants



J.A. Carlisle, D.M. Gruen, O. Auciello,
D. C. Mancini, S.R. Phillpot, L.A. Curtiss



T. A. Friedmann, M.T. Dugger, T.E. Buchheit,
M.P. de Boer



D.H. Lowndes, V.I. Merkulov



E.A. Stach



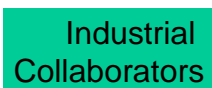
R. J. Nemanich



V.P. Dravid

R. Ruoff (NW)
R. Carpick (UW-Wisconsin)
R. J. Hamers (UW-Wisconsin)

Expressed interest in joining



Intel, Delphi, FlowServe, Second-Sight, IPLAS (TI,
Motorola, Fairchild Semi., Coventor, Corning
Intelli., Timken, John Crane, under discussion)



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

4

Management Plan

- Center coordinators
 - John Carlisle - ANL
 - Thomas Friedmann - SNL
- Funding - \$300K / Year
 - Three post docs and four graduate students
 - Post docs/Students to work on collaborative projects
 - \$15K - annual workshop
- Conference calls – Website (<http://chemistry.anl.gov/MSD/CSP.htm>)
- Annual workshop to recalibrate priorities/budget
- Kick-off meeting in April 2002



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

5

Budget

Institution	Funding (\$1,000's)	Type of Support	Task/Project
ANL	\$65 15	Postdoc Graduate Student (Theory)	Task 2B, 1A, 1B Task 2A
SNL	65	Postdoc	Task 1A, 1B
ORNL	65	Postdoc	Task 2B
LBNL	25	Graduate Student	Task 1B, 1A
NU	25	Graduate Student	Task 2B, 2A
NCSU	25	Graduate Student	Task 2A, 2B
All	15	Annual Workshop (coordinated by ANL/SNL)	All
TOTAL	\$300	\$285K Funding used to support postdocs, graduate students	



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

6

People

- ANL
 - Xingcheng Xiao, Michael Sternberg, Patrick Schelling
- SNL
 - ?
- ORNL
 - ?
- LBNL
 - Andy Minor, Chris Muhstein
- NW
 - S.Y. Li
- NCSU
 - Yunyu Wang



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

7

Project Tasks

- Two tasks focused on areas where basic understanding can be accelerated by teaming.
 - Task 1: Mechanical and Tribological Properties
 - Materials issues in carbon-based MEMS devices
 - Mechanical and tribological properties of carbon-based thin films
 - Task 2: Transport Properties
 - Electronic properties of carbon based materials
 - Carbon-based Nanocomposites
- Common theme
 - Understanding carbon-based materials at the micro- and nano-scales.

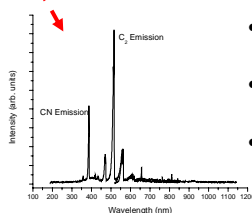


Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

8

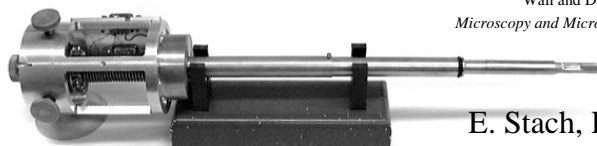
New ANL Microwave Plasma System



- New Plasma Chemistries
 - B, Al, P, etc.
- Higher Pressures
 - Faster deposition
- Larger Area
 - 100 mm wafers
 - UNCD-MEMS

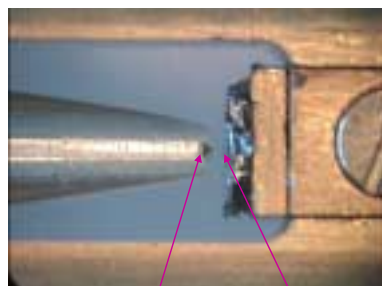
In-situ Nanoindentation TEM Holder

holder



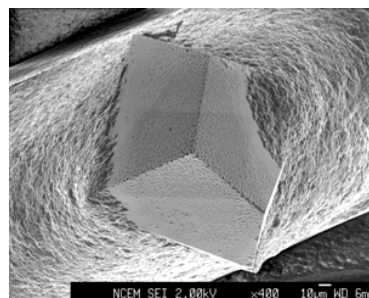
Wall and Dahmen,
Microscopy and Microanalysis, 3, 1997

E. Stach, LBNL



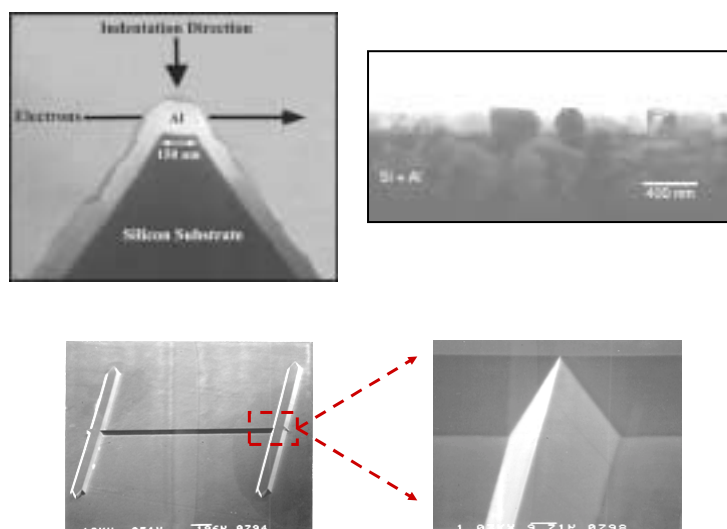
diamond

sample

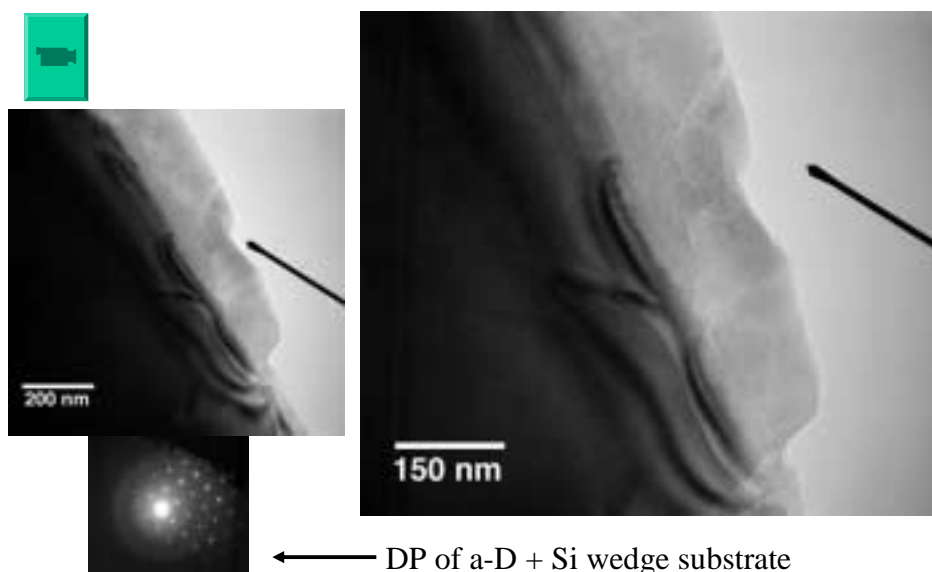


diamond indenter

Lithographically-prepared substrates

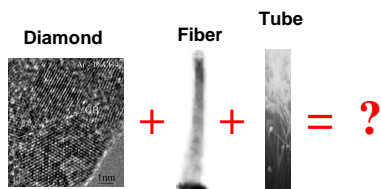


α -Diamond 1st indent post-indent stills

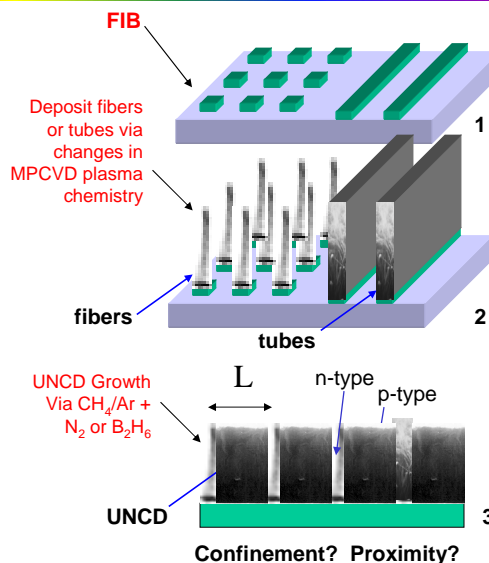


Carbon Nanocomposites

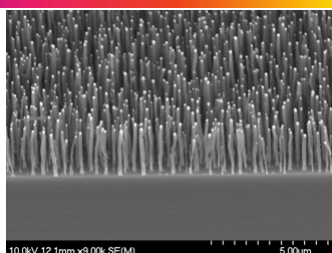
- What if one could *strategically* combine sp^3 and sp^2 -bonded carbon in a material?



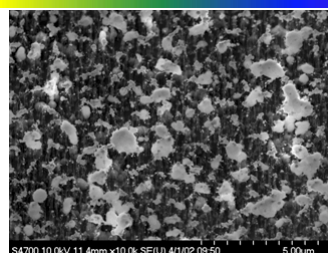
- UNCD/Nanofibers/Nanotubes: All synthesized via plasma CVD
 - Change plasma chemistry to control sp^3/sp^2 ratio and/or morphology
- Mechanical, Tribological, **Electrical**, Optical Properties?



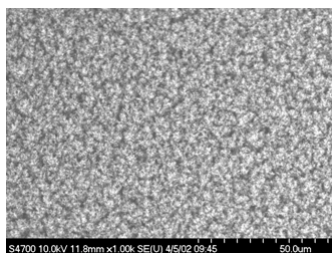
SEM Morphology of VACNF with UNCD



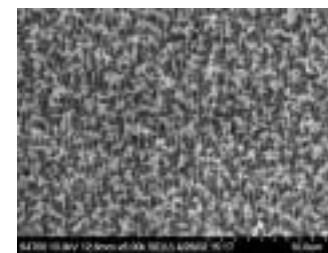
Before Deposition



Seeded, after deposition

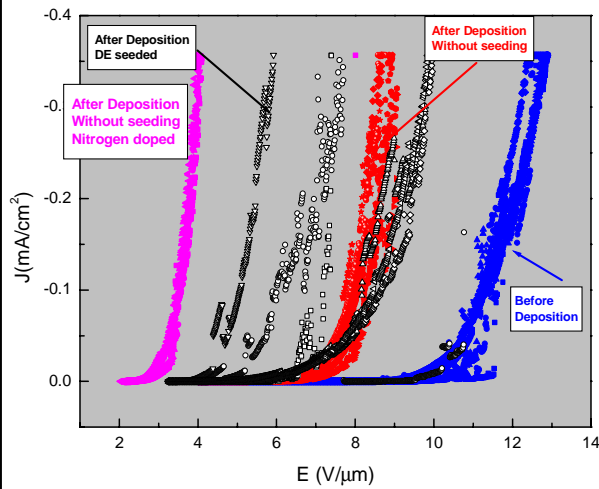


Without seeding, after deposition

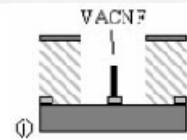
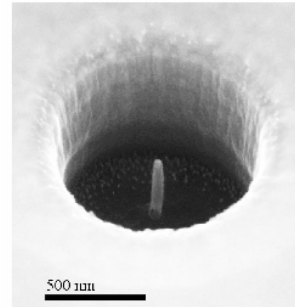


After deposition, Nitrogen doped

Field Emission Characteristics of CNF Forest with UNCD



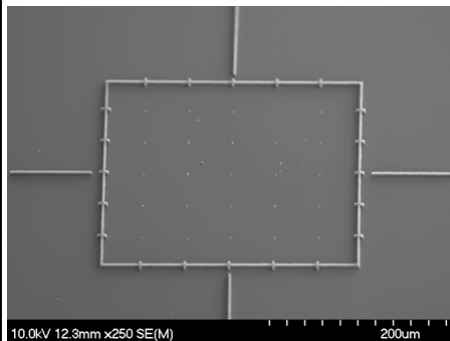
Current density-Field plots



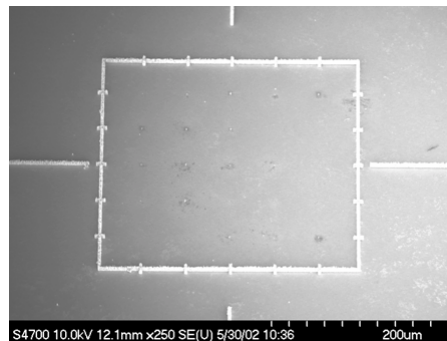
Gated VACNF Cathode Structure

Comparison of Separated Nanofibers Before and After Deposition

- Appropriate seeding process is the key step to deposit UNCD conformally on high aspect-ratio of CNF

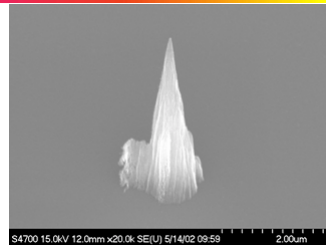


Before Deposition

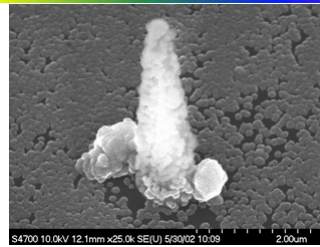


After Deposition

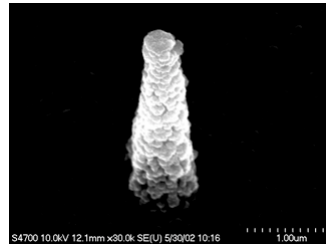
Single Nano Carbon Fibers Covered by UNCD



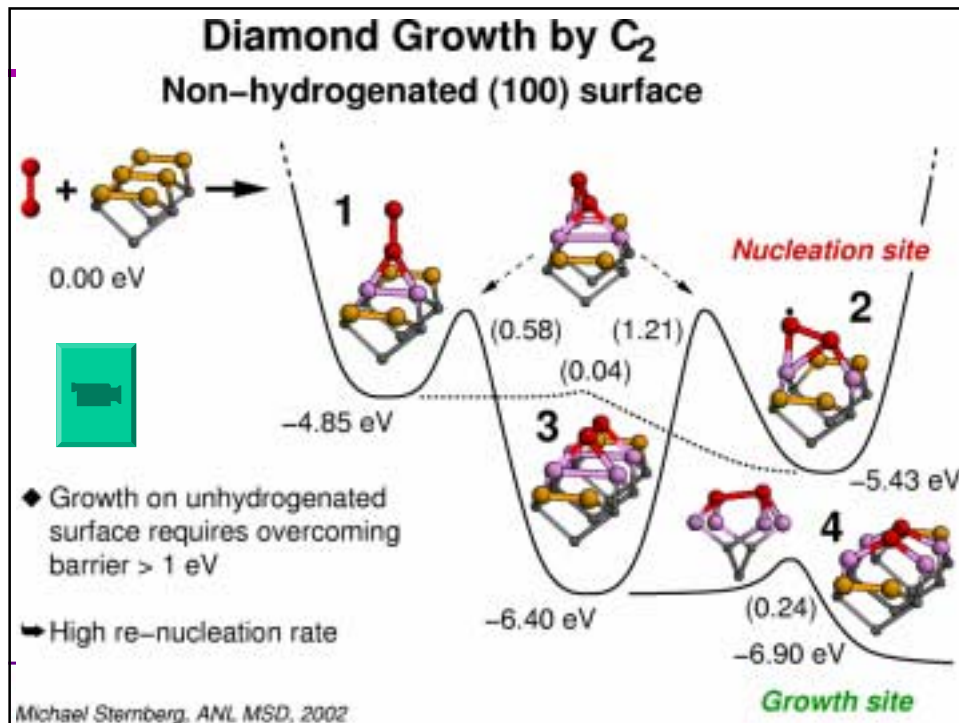
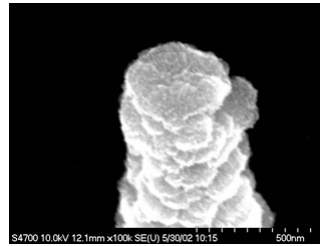
Before Deposition



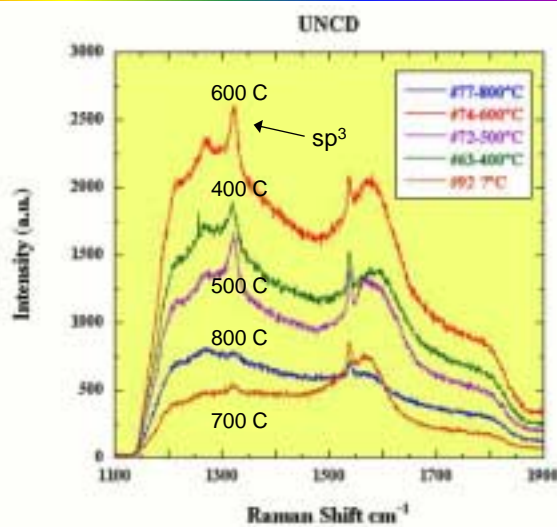
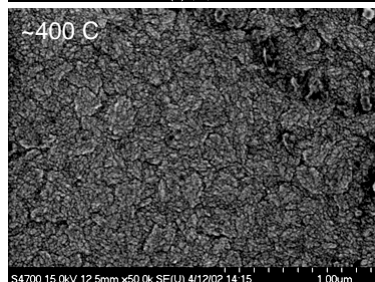
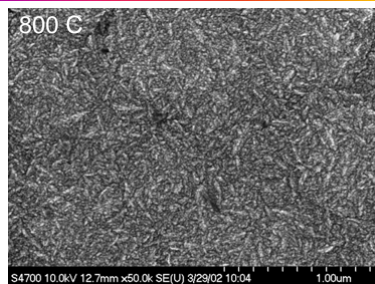
After Deposition



After Deposition, after seeding with nano diamond powders



Low Temperature Growth of UNCD



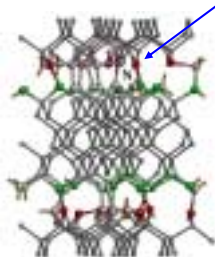
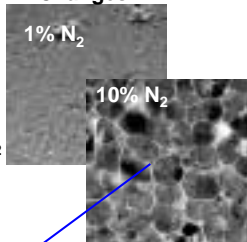
UV-Raman Spectroscopy

Nitrogen-Doped UNCD: Grain Boundary Conduction?



MPCVD Ar+CH₄+N₂
C₂, CN Precursors

Morphology Changes

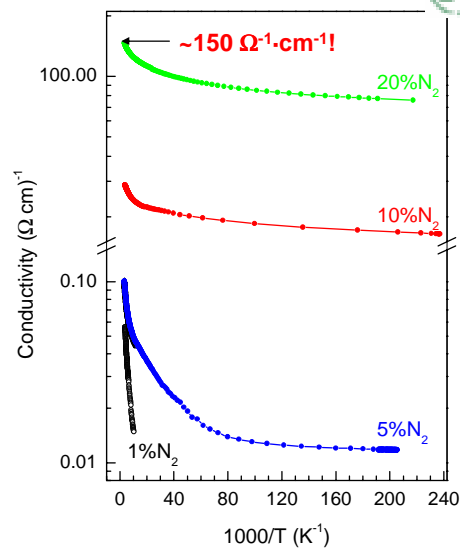


Nitrogen at GBs
favored by 4-5 eV

- GB Conduction?
- Morphology?

L.A. Curtiss (ANL)

J.A. Carlisle, O. Auciello, D.M. Gruen (ANL)



Nitrogen-Doped UNCD: TEAMING

R.J. Nemanich

NC STATE UNIVERSITY

PEEM
FEEM

Diamond: Neg.
Electron Affinity

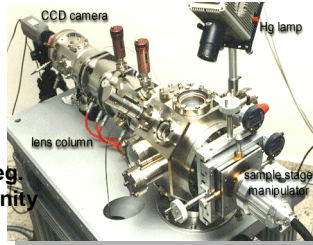
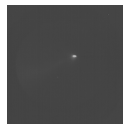
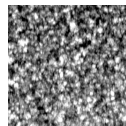


Image emission
sites in nitrogen-
doped UNCD:



Localized at GBs?

AFM

FEEM

V.P. David

NORTHWESTERN UNIVERSITY

TEM Holography

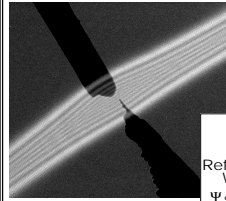
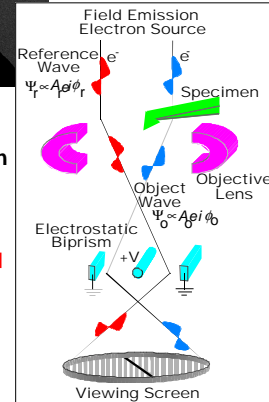


Image variation in
electric potential
in sample

Charge Localized
at GBs?



Materials Science Division
Advanced Materials Laboratory

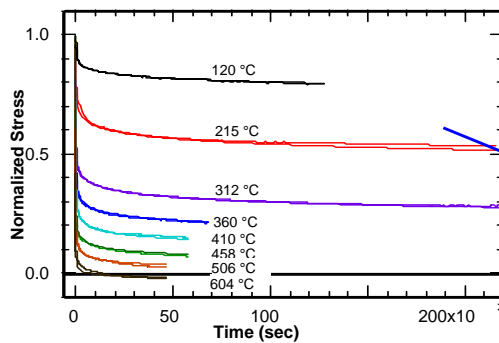
Carbon-based Nanostructured Materials
June 14, 2002

23

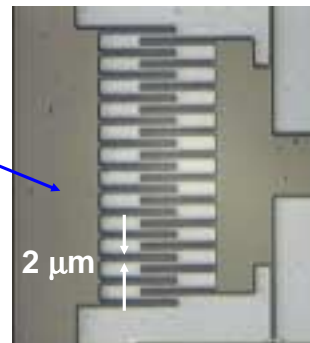
Diamond for MEMS: Thermal Budget a big issue!

$$\sigma(t, T) = \sigma_0 + \frac{\epsilon_{sp^2-sp^3}}{1-\nu} \int_0^\infty N(E_A) \{1 - \exp[-v_0 t \exp(-E_A / k_b T)]\} dE_A$$

T. A. Friedmann, (SNL)



Predictive model for stress relaxation
dynamics leads to strain control



Enables a-D MEMS devices

- Growth stresses controlled by annealing
- Use a-D devices as a probe of the nanoscale tribological behavior

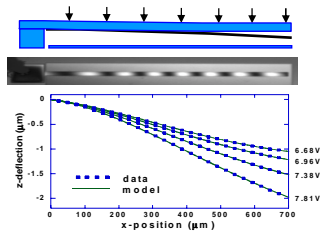
Materials Science Division
Advanced Materials Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

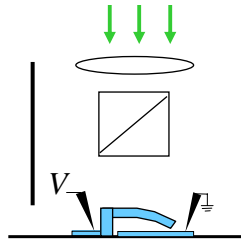
24

MEMS will be used to examine mechanical properties

Mechanical properties



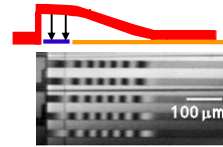
Metrology: Interferometry



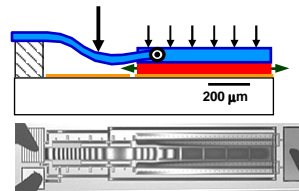
M. de Boer (SNL)



Adhesive properties



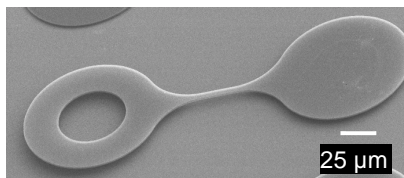
Frictional properties



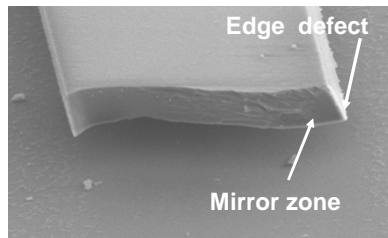
- Use interferometry and MEMS designs to probe materials properties

Fracture Mechanics at the micro scale.

Use lateral force capabilities of a Nanoindenter

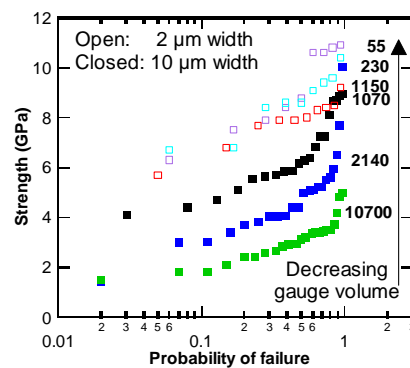


a-D microtensile sample



a-D Fracture surface

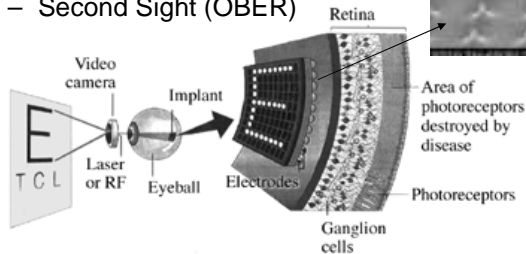
T.E. Buchheit T. A. Friedmann (SNL)



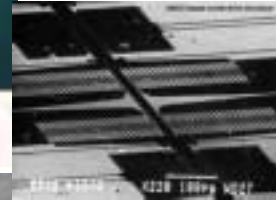
- Determine fracture mechanisms
- Explore limits of strength
- a-D and UNCD films
- Nanotubes (?)

Potential Technological Applications & Industrial Partners

- MPCVD
 - IPLAS
- MEMS
 - Intel, Delphi, TI, etc.. (WFO)
- Chemical Process Pumps
 - Flowserve (OIT-IMF)
- Bio-Electrodes
 - Second Sight (OBER)



UNCD Comb Drive



UNCD-Coated SiC Seal

Summary

- Scientific excellence
- Involvement of several laboratories
 - Brings together the top DOE programs in this area at DOE laboratories as well as universities
- Clear relationship to energy and DOE technologies
 - EE/transportation technologies - advanced electronics
 - EE/power technologies – power systems
 - Energy efficiency – mechanical pumps, sensors
 - Defense Program – advanced microsystems, sensors
- Partnerships with industry

Task 1A Materials Issues in Diamond-based MEMS

- Goal
 - Develop advanced understanding of carbon-based materials growth
 - Integrate carbon materials into devices for basic materials studies
- Team
 - SNL
 - synthesis and characterization of amorphous diamond films
 - design and fabrication of a-D and UNCD MEMS structure
 - ANL
 - synthesis and characterization of UNCD and ultra-low friction films
 - ORNL
 - growth of aligned carbon nanotubes and carbon nanocomposites
- Key Issues
 - Real world device fabrication
 - Integration strategies for hybrid materials combinations (e.g. UNCD with nanotubes or amorphous diamond)
 - Test vehicle design for nanoscale measurements



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

29

Task 1B Mechanical and Tribological Properties

- Goal
 - Understand the role of tribology (e.g. friction, adhesion, and wear) and fracture mechanics at the nanoscale in carbon-based structures.
- Team
 - SNL
 - Measurement of friction and wear at high shear rate
 - Fracture toughness and stiction in carbon-based MEMS
 - ANL
 - Computational chemistry for basic understanding of friction and wear
 - LBNL
 - in situ TEM imaging of defect/crack creation during nanoindentation
- Key Issues
 - Friction, wear and adhesion mechanisms in carbon MEMS
 - Fundamental limits of strength through control of defects
 - Mechanism of low friction in hydrogenated carbon films



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

30

Task 2A Nitrogen-Doped UNCD Films

- Goal
 - Understand the effect of nitrogen incorporation on the conductivity and field emission properties of UNCD thin films
- Team
 - ANL
 - Synthesis and characterization of nitrogen-doped UNCD films, Field emission studies, molecular dynamics calculations
 - NCSU
 - PEEM/FEEM studies of field emission properties
 - NU
 - TEM Holography studies to image charge at GBs, E-field of emitters
- Key issues
 - Grain boundary conduction/morphology in nitrogen-doped UNCD films
 - Field Emission properties of nitrogen-doped UNCD films



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

31

Task 2B Carbon Nanocomposites

- Goal
 - Synthesis of carbon nanofiber and hybrid nanofiber/diamond structures with unique mechanical, tribological, and electronic properties.
- Team
 - ORNL
 - Synthesis of vertically aligned carbon nanofiber arrays
 - ANL
 - Deposition of UNCD on nanofiber catalysts or pre-synthesized nanofiber arrays; Field Emission Studies
 - NCSU
 - PEEM/FEEM studies of field emission properties
- Key issues
 - Optimize growth of nanofiber array
 - Growth of UNCD/nanofiber/nanotube composites
 - Transport properties (electronic, field emission) of composites



Materials Science Division
Argonne National Laboratory

Carbon-based Nanostructured Materials
June 14, 2002

32